DECOMPOSITION OF NITROCOMPOUNDS IN THE PRESENCE OF ALUMINIUM CHLORIDE

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The thermal decomposition of different nitro-aromatic compounds, observed in the presence of anhydrous aluminium chloride, has been studied. The behaviour of these compounds is due to the nitro group introduced into the nucleus. Other substituents have also influence on the temperature of decomposition.

In our previous paper [1] the decomposition of nitrophenols and their esters, observed on heating in the presence of aluminium chloride, were reported. In the present work the decomposition of phenyl and mononitrophenyl esters of mononitrobenzoic acids, further that of other compounds were studied. It is shown by these experiments that the thermal decomposition observed is the consequence of the presence of the nitro substituent, for decomposition never occurred — under our experimental conditions — with compounds (phenols, carboxylic acids, phenolic esters) not containing nitro group (cf. Tables II, III, and previous paper Table I). Different substituents introduced into the same position on the nucleus of nitrobenzene may either reduce or increase the temperature of decomposition. Table II shows that alone 2-nitrobenzoic acid decomposed of the mononitrobenzoic acids, i. e. not alone the quality of the substituents but also their position have influence on the temperature of decomposition. It is to be noted that while among the mononitrophenols the ortho and para isomers, among the mononitrobenzoic acids the meta and para isomers behaved almost identically. Summing up all these the temperature of decomposition of the substituted nitrobenzene derivatives decreased in the following order:

$$3\text{-COOH} \simeq 4\text{-COOH} \simeq 3\text{-COOC}_6\text{H}_5 \simeq 4\text{-COOC}_6\text{H}_5 > 4\text{-Cl} > \text{nitrobenzene} >$$
$$> 3\text{-OH} > 2\text{-COOH} \simeq 4\text{-OH} \simeq 2\text{-OH} > 2\text{-COOC}_6\text{H}_5.$$

Among the studied nitro derivatives of phenyl benzoates the 2- and 4-nitrophenolic esters, and the esters of 2-nitrobenzoic acid decomposed at relatively low temperature (Table III). Compared this with the temperature of decomposition of mononitrophenols and mononitrobenzoic acids it can be concluded that esters, derived from phenols or acids easily decomposing, have also a relatively low temperature of decomposition.

Table I

	$AlCl_3$-comp. ratio	Comp. (g)	$AlCl_3$ (g)	Temp. of decomp. (°C)
Nitrobenzene	2:1	0,9	1,95	200
4-hydroxy-nitrobenzene	2:1	0,9	1,70	165
4-carboxy-nitrobenzene	2:1	0,9	1,44	—
4-chloro-nitrobenzene	2:1	0,9	1,53	204

Table II

	$AlCl_3$-acid ratio	Acid (g)	$AlCl_3$ (g)	Temp. of decomp. (°C)
Benzoic acid	2:1	0,9	1,97	—
2-Nitro-benzoic acid	2:1	0,9	1,44	166
3-Nitro-benzoic acid	2:1	0,9	1,44	—
4-Nitro-benzoic acid	2:1	0,9	1,44	—
Phenylacetic acid	2:1	0,9	1,76	—
Chloroacetic acid	2:1	0,9	2,55	—

Experimental[1]

Materials

Aluminium chloride anhydrous (B. D. H. preparate).
Benzoic acid, nitrobenzoic acids, phenylacetic acid, choloroacetic acid, phenylbenzoate, nitrobenzene and 4-chloro-nitrobenzene.
Commercial grade.
Nitrophenyl benzoates. 2-Nitrophenyl benzoate, m. p.: 54°; 3-nitrophenyl benzoate, m. p.: 93—95°; 4-nitrophenyl benzoate, m. p.: 142°.
Phenyl nitrobenzoates. Phenyl 2-nitrobenzoate, m. p.: 52—53°; phenyl 3-nitrobenzoate, m. p.; 95—97°; phenyl 4-nitrobenzoate, m. p.: 127—129°.
Nitrophenyl nitrobenzoates. 2-Nitrophenyl 2-nitrobenzoate, m. p.: 124—126°; 2-nitrophenyl 3-nitrobenzoate, m. p.: 128—130°; 2-nitrophenyl 4-nitrobenzoate, m. p.: 141—142°; 3-nitrophenyl 2-nitrobenzoate, m. p.: 113—114°; 3-nitro-

[1] Melting points are uncorrected.

phenyl 3-nitrobenzoate, m. p.: 130—131°; 3-nitrophenyl 4-nitrobenzoate, m. p.: 173—174°; 4-nitrophenyl 2-nitrobenzoate, m. p.: 111—112°; 4-nitrophenyl 3-nitrobenzoate, m. p.: 141—142°; 4-nitrophenyl 4-nitrobenzoate, m. p.: 155—157°. Esters, mentioned above, were prepared from the corresponding sodium phenolates and benzoyl clorides in benzene.

Determination of temperature of decomposition was the same as discribed in the previous paper [1].

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Table III

	AlCl-ester ratio	Ester (g)	$AlCl_3$ (g)	Temp. of decomp. (°C)
Phenyl benzoate	2:1	0,9	1,20	—
Phenyl 2-nitrobenzoate	2:1	0,9	0,98	82
Phenyl 3-nitrobenzoate	2:1	0,9	0,98	—
Phenyl 4-nitrobenzoate	2:1	0,9	0,98	—
2-Nitrophenyl benzoate	2:1	0,9	0,98	129
2-Nitrophenyl 2-nitrobenzoate	2:1	0,9	0,83	120
2-Nitrophenyl 3-nitrobenzoate	2:1	0,9	0,83	128
2-Nitrophenyl 4-nitrobenzoate	2:1	0,9	0,83	128
3-Nitrophenyl benzoate	2:1	0,9	0,98	193
3-Nitrophenyl 2-nitrobenzoate	2:1	0,9	0,83	125
3-Nitrophenyl 3-nitrobenzoate	2:1	0,9	0,83	194
3-Nitrophenyl 4-nitrobenzoate	2:1	0,9	0,83	195
4-Nitrophenyl benzoate	2:1	0,9	0,98	132
4-Nitrophenyl 2-nitrobenzoate	2:1	0,9	0,83	118
4-Nitrophenyl 3-nitrobenzoate	2:1	0,9	0,83	143
4-Nitrophenyl 4-nitrobenzoate	2:1	0,9	0,83	144

Reference

[1] *Furka, Á., T. Széll:* Acta Phys. et Chem. Szeged 6, 116 (1960).

РАЗЛОЖЕНИЕ НИТРОСОЕДИНЕНИЙ В ПРИСУТСТВИИ ХЛОРИСТОГО АЛЮМИНИЯ

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Было изучено разложение различных нитро-ароматических соединений, наблюдаемое в присутствии хлористого алюминия. Такое поведение этих соединений является следствием введения в ароматическое ядро ниро-группы. Другие заместители кольца также влияют на температуру разложения.